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**(54) ACRYLIC BLOCK COPOLYMER, COMPOSITION FOR VIBRATION- DAMPING MATERIAL, AND PRODUCTION METHOD FOR ACRYLIC BLOCK COPOLYMER**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an acrylic block copolymer which always exhibits vibration-damping properties with a constant level or higher over a wide temperature range and can be widely used in various fields, a composition for vibration-damping materials containing the same, and a method capable of easily and efficiently producing the acrylic block copolymer.

SOLUTION: This acrylic block copolymer is prepared by copolymerizing at least two sets of monomer components different in composition in the presence of a polyvalent (at least trivalent) mercaptan compound. Over a temperature width of at least 90°C in the range of -50°C to 150°C, the loss tangent ( $\tan\delta$ ) of the block copolymer is 0.3 or higher. The block copolymer contains 55 wt.% or higher repeating units derived from a (meth)acrylic monomer, the total repeating unit content being 100 wt.%.

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**CLAIMS**

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[Claim(s)]

[Claim 1] While it is the acrylic block copolymer which comes to give 2 or more sets of monomer components of a different presentation a polymerization reaction under existence of the multiple-valued mercaptans more than trivalent and a loss tangent ( $\tan\delta$ ) is -50-150 degrees C The repeat unit which is 0.3 or more and constitutes this acrylic block copolymer over temperature width of face of 90 degrees C or more The acrylic block copolymer characterized by the repeat unit formed of an acrylic (meta) monomer being 55 % of the weight or more if all repeat units are made into 100 % of the weight.

[Claim 2] It is the acrylic block copolymer which comes to give 2 or more sets of monomer components of a different presentation a polymerization reaction under existence of the multiple-valued mercaptans more than trivalent. The maximum difference of the glass transition point on count of each polymer obtained when 2 or more sets of monomer components of a presentation carry out the polymerization of each monomer component is 130-200 degrees C. this -- \*\* -- This acrylic block copolymer is 35 - 65% of the weight of the rate that the weight of the \*\*\*\*\* component first given to a polymerization reaction occupies to 100 % of the weight of AUW of all monomer components. The acrylic block copolymer characterized by obtaining as indispensable \*\*\*\*\* which gives the different following monomer component from the monomer component first given to the polymerization reaction to a polymerization reaction while the conversion of the monomer component first given to the polymerization reaction is less than 45%.

[Claim 3] When it is the constituent for sound deadeners which comes to contain an acrylic block copolymer according to claim 1 or 2 and the content of this acrylic block copolymer makes this constituent for sound deadeners 100 % of the weight, it is the constituent for sound deadeners characterized by being 10 % of the weight or more.

[Claim 4] It is the manufacture approach of the acrylic block copolymer which comes to contain the \*\*\*\*\* reaction process which gives 2 or more sets of monomer components of a different presentation to a polymerization reaction under existence of the multiple-valued mercaptans more than trivalent. The maximum difference of the glass transition point on count of each acrylic polymer obtained when 2 or more sets of monomer components of a presentation carry out the polymerization of each monomer component ( $T_g$ ) is 130-200 degrees C. this -- \*\* -- The weight of the monomer component from which the polymer with which  $T_g$  on count becomes 50 degrees C or more is obtained is 35 - 65% of the weight of the rate of occupying to 100 % of the weight of AUW of all monomer components. This polymerization reaction process The manufacture approach of the acrylic block copolymer characterized by performing as indispensable \*\*\*\*\* which gives the different following monomer component from the monomer component first given to the polymerization reaction to a polymerization reaction while the conversion of the \*\*\*\*\* component first given to a polymerization reaction is less than 45%.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention relates to the manufacture approach of the constituent for sound deadeners containing an acrylic block copolymer and this acrylic block copolymer, and an acrylic block copolymer.

**[0002]**

**[Description of the Prior Art]** The constituent for sound deadeners is a constituent which forms the high-damping material used in order to avoid that faults, such as destruction and damage, arise in an equipment, a building, etc. by transfer of vibration, for example, it is used as the constituent which forms the sheet of rubber or an asphalt system, or a coating, and also it is applied as a resin constituent for forming a sandwiches steel plate etc. In usual, the high-damping material formed from such a constituent for sound deadeners can be constituted considering polymeric materials as indispensable, can absorb the vibrational energy from the outside using internal friction by the viscoelastic property of polymeric materials, and can demonstrate the vibration-deadening engine performance by changing into heat energy and attenuating vibration.

**[0003]** By the way, in order to show the highest energy-absorbing effectiveness in the glass transition point (T<sub>g</sub>) field of polymeric materials, the temperature requirement which demonstrates the viscoelastic property of a high-damping material by this was decided by such constituent for sound deadeners, and crossing to large temperature requirements other than T<sub>g</sub> field, and demonstrating the high vibration-deadening engine performance had with it the problem of being difficult. If the temperature requirement which can demonstrate the vibration-deadening engine performance is wide, since the high vibration-deadening engine performance can be demonstrated under various environmental conditions, it will become possible to make it apply broadly in various kinds of fields, such as an automobile, a building, a vessel, and electrical and electric equipment, for example.

**[0004]** In JP,5-272588,A, two kinds of macromolecules while T<sub>g</sub> is -10-40 degree C are compound-ized, the sound deadener which added the filler is indicated, and the aqueous resin dispersant which comes to contain in JP,9-111132,A two kinds of heart-husks type complex particles which have the core (core part) from which it differs while T<sub>g</sub> is -10-50 degree C, and the polymer particle which has specific T<sub>g</sub> is indicated. However, with these techniques, the problems without enough and thermal resistance that the production process of compound-izing of a macromolecule is complicated and that it was uneconomical were in the top where the temperature requirement which shows the vibration-deadening engine performance in practical temperature is narrow.

**[0005]** It is indicated that the vibration-deadening engine performance which was excellent when a photograph INIFATA polymer was a homopolymer or a random copolymer is shown in the Patent Publication Heisei No. 505431 [ seven to ] official report about the ultraviolet-rays hardenability acrylate pressure sensitive adhesive constituent which used the photograph INIFATA polymer. However, a production process is complicated and there was a problem that the photograph INIFATA polymer obtained became expensive. Furthermore, there was room of the device for making it apply

broadly in various kinds of fields by raising the mechanical physical properties of a photograph INIFATA polymer.

[0006] The acrylic block copolymer formed from the styrene system or (meta) the acrylic block whose Tg is 50 degrees C or more, and the acrylic block whose Tg is 30 degrees C or less (meta) (meta) is indicated by JP,6-287253,A. However, when Tg of each block is separated, the vibration-deadening engine performance in the intermediate-temperature field is inferior, when Tg of each block is near, the vibration-deadening engine performance by the side of low temperature and an elevated temperature will be inferior, and there was room of the device for crossing to a large temperature requirement and demonstrating the high vibration-deadening engine performance. furthermore, the polymer currently indicated here -- a jib -- it was lock structure and was what is inferior to mechanical physical properties as compared with the block polymer which has triblock structure, the star type block structure, and the multi-block structure.

[0007] It is indicated by JP,5-125252,A that the high vibration-deadening engine performance is shown in the triblock copolymer which has a vinyl aromatic compound polymer block, the polymer (\*\*) block of conjugated diene, and the taper block that a vinyl aromatic compound increases gradually among a vinyl aromatic compound and conjugated diene, and its hydrogenation object in a -50-80-degree C temperature requirement about vibration deadening and the constituent for insulators which blended the softener, the binder, and the bulking agent. However, the triblock copolymer was the structure of having a double bond, since the hydrogenation object also had a residual double bond, thermal resistance and weatherability were not enough and there was room of the device for making it apply broadly in various kinds of fields by fully raising such fundamentality ability.

[0008] It is indicated by carrying out the polymerization of the low Tg component to JP,4-312238,A previously, and performing an acrylic emulsion polymerization to it under existence of diene system rubber about the graft polymer obtained by subsequently dropping two steps of high Tg components that the shock resistance in the low temperature of the graft polymer obtained improves. However, in this graft polymer, since it was a random copolymer, neither the vibration-deadening engine performance nor a mechanical strength was enough, and when an emulsion polymerization was performed, there was a problem that a production process is complicated and that it was uneconomical.

[0009] A multiple-valued mercaptan is used for JP,8-188631,A, and it is indicated that functionality, such as a mechanical strength, can be raised without starting phase separation about the thermoplastic addition polymer from which the presentation of a copolymer part is changing continuously though it is a block polymer. However, although the copolymer part was constituted from this thermoplastic addition polymer by the hard component and the software component, since the hard component ran short of the hard components currently indicated with 30% of polymer, the cohesive force of a polymer was insufficient, and the room of amelioration was in the vibration-deadening engine performance and mechanical physical properties. Furthermore, the temperature requirement where a hard component shows the vibration-deadening engine performance which Tg of the software component used by the polymerization raised with -19 degree C, and came out, and the Tg range of a polymer became 0-85 degrees C for a certain reason, and was excellent in this polymer although 50% of polymer was also indicated, i.e., the temperature requirement where  $\Delta$  shows 0.3 or more, was only the bottom of 5-90 degrees C and a comparatively hot environment. Therefore, in order to obtain the polymer in which the vibration-deadening engine performance which was more excellent also in the bottom of a low-temperature environment is shown, the device was needed further. Furthermore, although 50% of the hard component was constituted from this polymer by styrene, when styrene was used by the polymerization, since chain transfer was intense, the fault that it was bad and the vibration-deadening engine performance and mechanical physical properties could not improve easily also had the generation effectiveness of block polymer. With the technique indicated by JP,8-188631,A, there was room of the device for crossing to a large temperature requirement and demonstrating the high vibration-deadening engine performance like the above.

[0010]

[Problem(s) to be Solved by the Invention] In view of the above, this invention is crossed to a broad

temperature requirement, always shows the vibration-deadening engine performance more than fixed, and aims at offering the constituent for sound deadeners containing the acrylic block copolymer which can be made to apply broadly in various kinds of fields, and this acrylic block copolymer, and the manufacture approach that this acrylic block copolymer is efficiently [ easily and ] producible.

[0011]

[Means for Solving the Problem] While this invention is an acrylic block copolymer which comes to give 2 or more sets of monomer components of a different presentation a polymerization reaction under existence of the multiple-valued mercaptans more than trivalent and a loss tangent ( $\tan\delta$ ) is -50-150 degrees C The repeat unit which is 0.3 or more and constitutes the above-mentioned acrylic block copolymer over temperature width of face of 90 degrees C or more When all repeat units are made into 100 % of the weight, the repeat unit formed of an acrylic (meta) monomer is the acrylic block copolymer which is 55 % of the weight or more.

[0012] The time that this invention person etc. examines many things about the polymeric materials which show the vibration-deadening engine performance, It first notes that the loss tangent ( $\tan\delta$ ) in dynamic viscoelasticity measurement serves as a guide of the vibration-deadening engine performance of polymeric materials. Moreover, by specifying the property shown by  $\tan\delta$  also paying attention to an acrylic block copolymer being suitable as polymeric materials which show the vibration-deadening engine performance, and specifying the configuration of the repeat unit of an acrylic block copolymer It found out that it could consider as the constituent for sound deadeners which can be made to apply broadly in various kinds of fields, and hit on an idea for the above-mentioned technical problem to be splendidly solvable. Moreover, if the glass transition point ( $T_g$ ) of the block chain of an acrylic block copolymer is changed continuously or gradually, it will also find that the property shown by  $\tan\delta$  can be carried out as a request, and this invention will be reached. Below, this invention is explained in full detail.

[0013] The acrylic block copolymer of this invention is an acrylic block copolymer which comes to give 2 or more sets of monomer components of a different presentation a polymerization reaction under existence of the multiple-valued mercaptans more than trivalent, and while a loss tangent ( $\tan\delta$ ) is -50-150 degrees C, it is 0.3 or more over temperature width of face of 90 degrees C or more. An acrylic block copolymer means the block copolymer formed of the monomer component which makes an acrylic (meta) monomer indispensable.

[0014] It is [ be / it / under / this / specification / setting ] the semantics of one monomer component constituted by one sort or two sorts or more of monomers in 1 set in 2 or more sets of monomer components. Moreover, when 2 or more sets of monomer components of a different presentation mean using at least 2 sets of different monomer components, for example, it uses 3 or more sets of monomer components, there may be combination one group and other one group of whose are the same monomer components, and there may not be such a combination.

[0015] In this invention, a loss tangent ( $\tan\delta$ ) is used as an index which shows the vibration-deadening engine performance of polymeric materials. A loss tangent ( $\tan\delta$ ) is a value which is acquired by dynamic viscoelasticity measurement and acquired by  $\tan\delta$  (ing) a loss modulus with a storage modulus. The value of  $\tan\delta$  becomes so large that the rate of having made the elastic modulus losing is large. Since it is making an elastic modulus lose, i.e., damping, the vibration-deadening engine performance will be excellent, so that the value of  $\tan\delta$  is large. In addition, specifically, the frequency of 10Hz, 0.2% of strains, the approach of measuring by part for programming-rate/of 3 degrees C, etc. are applied suitably, using the dynamic viscoelasticity measuring instrument "RDAII" (trade name) by the REOMETO Rix Far East company as a measuring method of dynamic viscoelasticity.

[0016] While the above-mentioned loss tangent ( $\tan\delta$ ) is -50-150 degrees C, two kinds indicated following (1) and (2) in the  $\tan\delta$  curve which plotted  $\tan\delta$  [ in / that it is 0.3 or more / for temperature / the temperature ] at the axis of ordinate on an axis of abscissa of cases are meant over temperature width of face of 90 degrees C or more.

(1) When the temperature width of face whose  $\tan\delta$  is 0.3 or more includes 90 degrees C or more

continuously.

(2) Although the temperature width of face whose  $\tan\delta$  is 0.3 or more is discontinuous and there is, when the sum total of the temperature width of face two or more  $\tan\delta$  of whose is 0.3 or more includes 90 degrees C or more. [ two or more ]

[0017] As an example in the above (1),  $\tan\delta$  increases, 0.3 is exceeded at -20 degrees C, for example, and the case where it is 0.3 or more continuously etc. is mentioned to 80 degrees C. In this case, while  $\delta$  is -20-80 degree C of  $\tan(s)$ , it is 0.3 or more over temperature width of face of 100 degrees C. It may not be limited especially as a configuration of a  $\tan\delta$  curve, for example, the increment in monotone may be carried out, you may decrease from the middle, and increase and decrease may be repeated repeatedly.

[0018] As an example in the above (2), the  $\tan\delta$  curve increases, and 0.3 is exceeded at -20 degrees C, and it decreases after that, becomes less than 0.3 at 30 degrees C, it increases again, for example, 0.3 is exceeded at 50 degrees C, and the case where it becomes 0.3 or more to 100 degrees C etc. is mentioned. In this case, while  $\delta$  is -20-30 degree C of  $\tan(s)$ , and 50-100 degrees C, it is 0.3 or more over 50 degrees C [ temperature width of face of 50 degrees C, and ] a total of 100 degrees C. It is not limited especially like the case of the above (1) as a configuration of a  $\tan\delta$  curve.

[0019] When the vibration-deadening engine performance is uniformly called for at all the temperature between -50-150 degrees C the above (1) and in the case of (2), preferably, the vibration-deadening engine performance in a certain specific temperature requirement is especially strong, the case of (1) is demanded, and, sometimes, the vibration-deadening engine performance of other temperature requirements has the to some extent desirable case of (2).

[0020] While  $\delta$  is -30-130 degree C of  $\tan(s)$  in an acrylic block copolymer in this invention, it is desirable that it is 0.3 or more over temperature width of face of 100 degrees C or more. More preferably, while  $\delta$  is -30-110 degree C of  $\tan(s)$ , it is 0.3 or more over temperature width of face of 110 degrees C or more. Most preferably, while  $\delta$  is -30-150 degree C of  $\tan(s)$ , it is 0.5 or more over temperature width of face of 110 degrees C or more. Moreover, when the part which becomes 0.3 or more in a temperature requirement 0 degree C or less is contained, it is desirable, when the part which becomes 0.4 or more is contained, it is still more desirable, and it is desirable especially when the part which becomes 0.5 or more is contained.

[0021] When the repeat unit which constitutes the acrylic block copolymer of this invention makes all repeat units 100 % of the weight, the repeat unit formed of an acrylic (meta) monomer is 55 % of the weight or more. Fundamentality ability, such as the thermal resistance of an acrylic block copolymer and weatherability, will fall that it is less than 55 % of the weight. More preferably, it is 70 % of the weight or more, and is 90 % of the weight or more still more preferably.

[0022] It will not be limited especially if it is \*\*\*\*\* given to a polymerization reaction under existence of the multiple-valued mercaptans more than trivalent as an approach of manufacturing the acrylic block copolymer of this invention, using 2 or more sets of monomer components of a different presentation. It is most suitable to manufacture as simplest technique, so that it may state below.

[0023] This invention is an acrylic block copolymer which comes to give 2 or more sets of monomer components of a different presentation a polymerization reaction under existence of the multiple-valued mercaptans more than trivalent again. The maximum difference of the glass transition point on count of each polymer obtained when 2 or more sets of monomer components of a presentation different the account of a top carry out the polymerization of each monomer component is 130-200 degrees C. The above-mentioned acrylic block copolymer is 35 - 65% of the weight of the rate (preferably) that the weight of the \*\*\*\*\* component first given to a polymerization reaction occupies to 100 % of the weight of AUW of all monomer components. The conversion of the monomer component which is 43 - 57 % of the weight, and was first given to the polymerization reaction still more preferably 40 to 60% of the weight is less than (preferably) 45%. While being 20 - 40%, the monomer component first given to the polymerization reaction is also the acrylic block copolymer obtained considering \*\*\*\*\* which gives the different following monomer component to a polymerization reaction as indispensable. It is possible to cross to a broad temperature requirement, and for the vibration-deadening engine

performance more than fixed to always be shown, and to make it apply broadly in various kinds of fields from having the block chain to which the glass transition point (Tg) was changed continuously or gradually in such an acrylic block copolymer.

[0024] The glass transition point on count of the polymer obtained when the polymerization of the monomer component is carried out into this specification (Tg) means the calculated value calculated from following type \*\*, when the monomer component A comes to contain Monomers A1, A2, ..., An.

[0025]

$1/TgA = (a1 / 100) \times (1/TgA1) + (a2 / 100) \times (1/TgA2) + \dots$  The inside of a  $+(an/100) \times (1/TgAn)$  \*\* type, and TgA Tg on count of the polymer obtained by carrying out the polymerization of the monomer component A (K) is expressed. a1, and a2, ..., an Weight % of Monomers A1, A2, ..., An is expressed using a monomer component as 100 % of the weight. Namely,  $A1+A2+ \dots +An$  is 100 % of the weight. TgA1, TgA2, ..., TgAn express Tg (K) of the homopolymer of Monomers A1, A2, ..., An. Moreover, TgA of the monomer component A from which the polymer which has highest Tg is obtained in 2 or more sets of monomer components of a presentation which is different that the maximum difference of Tg on count of each polymer obtained when the polymerization of each monomer component is carried out is 130-200 degrees C TgB of the monomer component B from which the polymer which has lowest Tg is obtained I hear that there are 130 degrees C - 200 degrees C of differences, and there are. For example, if Tg(s) on count of the polymer obtained when the polymerization of the monomer components A, B, and C is carried out, respectively are 100 degrees C, 50 degrees C, and -50 degrees C, the maximum difference of Tg on count is 150 degrees C between A-C. About especially the difference between A-B (50 degrees C) and between B-C (100 degrees C), it is desirable to make it be the same as that of the case where 3 or more sets of monomer components which it is not limited and were mentioned above are used.

[0026] In the above-mentioned acrylic block copolymer, two points, the following (b) and (b), are mentioned as a reason Tg of a block chain will change continuously or gradually. Namely, while the monomer presentation in a (b) polymerization system changes continuously or gradually, when a polymerization advances From that the block chain formed from various monomer presentations arises, and Tg(s) of each polymer obtained from 2 sets of monomer components of a different presentation at least among each monomer component used (b) differing The block copolymer from which Tg of the block chain to generate changed continuously or gradually will be obtained at the same time a monomer presentation changes like (b).

[0027] If distribution of Tg of a block polymer is broad in order that vibrational energy may be absorbed well, namely, tandelta may show a large value in a temperature requirement with the block chain near each Tg with which Tg(s) differ as a reason the block copolymer from which Tg of the above-mentioned block chain changed continuously or gradually will be brought into a broad temperature requirement, and will always show the vibration-deadening engine performance more than fixed, it is because tandelta shows a large value in so broad a temperature requirement. Moreover, the vibration frequency of the energy which can absorb a polymer changes with the maneuverability of a polymer. The maneuverability of a polymer has the close relation to Tg, and generally, the higher polymer of Tg has worse maneuverability and it is [ maneuverability ] better. [ of the lower polymer of Tg ] Therefore, since the block copolymer from which Tg of a block chain changed continuously as mentioned above can absorb the energy of the vibration frequency according to the maneuverability of each block chain, it becomes possible [ absorbing vibration of various vibration frequency, such as 10-500 etc.Hz, for example ].

[0028] While a loss tangent (tandelta) is -50-150 degrees C in the above-mentioned acrylic block copolymer, it is desirable that it is 0.3 or more over temperature width of face of 90 degrees C or more. It can be performed more certainly that this crosses to a broad temperature requirement and the vibration-deadening engine performance more than fixed is always shown. Moreover, the same [ with having mentioned above ] as a repeat unit which constitutes an acrylic block copolymer, although various kinds of monomers can be used as a monomer which will constitute an acrylic block copolymer, when all repeat units are made into 100 % of the weight, it is desirable that the repeat unit formed of an



acrylic (meta) monomer is 55 % of the weight or more. This becomes the thing excellent in fundamentality ability, such as the thermal resistance of an acrylic block polymer, and weatherability, and making it apply broadly in various kinds of fields, such as an automobile, a building, a vessel, and electrical and electric equipment, can be performed more certainly.

[0029] When obtaining the above-mentioned acrylic block copolymer, in order to consider as the block polymer in which the tandelta curve more than fixed is continuously shown like the above (1), it is desirable that a monomer component is dropped duly and it is made to advance a polymerization at the process of a polymerization while a monomer component is dropped duly. Moreover, in order to obtain the block polymer in which a discontinuous tandelta curve is shown like the above (2), it is desirable to perform a polymerization by the technique of, interrupting dropping of the dropped monomer component on the way for example, advancing a polymerization for a while, and starting dropping again after that. If it does in this way, since presentation change of a polymerization system becomes discontinuous, the presentation of the block chain to generate will serve as discontinuity and distribution of Tg of a block chain will become discontinuous, it becomes discontinuous [ a tandelta curve ].

[0030] It is not limited especially as the above-mentioned (meta) acrylic monomer. For example, carboxyl group content (meta) acrylic monomer; (meta) acrylic-acid hydroxyethyl, such as an acrylic acid (meta), (Meta) hydroxy group content (meta) acrylic monomers [, such as acrylic-acid hydroxypropyl, ]; (meta) -- glycidyl group content (meta) acrylic monomers [, such as metaglycidyl acrylate, ]; (meta) -- acrylic-acid methoxy ethyl -- Alkoxy alkyl ester group content (meta) acrylic monomers, such as acrylic-acid ethoxyethyl; (meta) A methyl acrylate, (Meta) An ethyl acrylate, butyl acrylate (meta), acrylic-acid (meta) cyclohexyl, (Meta) 2-ethylhexyl acrylate, acrylic-acid (meta) n-octyl, (Meta) The acrylic monomer which has the alkyl ester group of the carbon atomic numbers 1-30, such as acrylic-acid lauryl and acrylic-acid (meta) stearyl, (meta); (Meta) One sort, such as JI (meta) acrylic monomers, such as JI (meta) acrylic-acid tetraethylene glycol, or two sorts or more are mentioned. the inside of these (meta) acrylic monomer -- the operating weight of a JI (meta) acrylic monomer -- 100 % of the weight of total monomer weight -- since the cohesive force of a polymer increases that it is 0.2 - 2 % of the weight preferably according to bridge formation and the vibration-deadening engine performance and mechanical physical properties improve 0.1 to 10% of the weight, it is desirable.

[0031] As repeat units other than the repeat unit formed of the above-mentioned (meta) acrylic monomer, the repeat unit formed from one sort of an acrylic monomer and a monomer which can be copolymerized (meta) which is indicated below, or two sorts or more is mentioned, for example. The styrene monomer represented by alpha methyl styrene, vinyltoluene, styrene, etc.; The methyl vinyl ether, Vinyl ether system monomers, such as ethyl vinyl ether and isobutyl vinyl ether; A fumaric acid, The monoalkyl ester of a fumaric acid, the dialkyl ester of a fumaric acid, The monoalkyl ester of a maleic acid and a maleic acid, the dialkyl ester of a maleic acid, Unsaturated carboxylic acid, such as monoalkyl ester of an itaconic acid and an itaconic acid, and dialkyl ester of an itaconic acid, and ester of those; (meta) Acrylonitrile, A butadiene, an isoprene, a vinyl chloride, a vinylidene chloride, vinyl acetate, a vinyl ketone, vinylpyridine, vinyl pyrrolidone, vinylcarbazole, etc. However, if it is that of a lifting or a cone and chain transfer is used so much, the generation effectiveness of block polymer will fall, and the vibration-deadening engine performance and mechanical physical properties of styrene may be unable to improve easily. As for the operating weight of styrene, it is desirable that it is [ of 100 % of the weight of total monomer weight ] 0 - 20 % of the weight preferably zero to 30% of the weight.

[0032] Although 2 or more sets of monomer components of a different presentation are used in order to obtain the above-mentioned acrylic block copolymer, it has broad Tg distribution as the maximum difference of Tg on count of each polymer obtained when the polymerization of each monomer component is carried out is 130 degrees C or more, and the polymer in which the vibration-deadening engine performance is shown in a large temperature requirement will be obtained. Moreover, if it exceeds 200 degrees C, it will be hard coming to prepare 2 or more sets of monomer components of a different presentation. More preferably, it is 130-180 degrees C, and is 150-180 degrees C still more preferably. It is desirable that Tg on count of 1 set which Tg on count of the polymer obtained, for

example as a gestalt with 2 or more sets of desirable monomer components of such a different presentation when the polymerization of the monomer component is carried out becomes -below 20 degrees C (253K), and the polymer obtained when the polymerization of the monomer component is carried out presupposes that the others which become more than 70 degree C (343K) are indispensable 1 set. It is suitable to set up so that it may become the maximum difference of Tg in 2 or more sets of monomer components of a different presentation used in order that the difference of Tg in 2 sets of such monomer components may obtain an acrylic block copolymer. The account of a top moreover, in using the 3rd set of monomer components other than 2 sets of monomer components of a different presentation It is desirable to set up so that it may become near the middle of Tg on count of each polymer obtained when the polymerization of 2 sets of monomer components of a presentation which is not limited especially as Tg on count of the polymer obtained when the polymerization of the 3rd set of monomer components is carried out, for example, is different the account of a top is carried out, respectively. furthermore, in using the 4th set of monomer components The difference of Tg of the monomer component used as the monomer component used as lowest Tg, and Tg low to the 2nd, It is desirable to set up so that each of the difference of Tg of the monomer component used as the monomer component which serves as low Tg the 2nd, and Tg low to the 3rd, and the difference of Tg of the monomer component used as the monomer component used as Tg low to the 3rd and highest Tg may become equal. It is also the same as when using 5 or more sets of monomer components.

[0033] When each monomer component is made into 100 % of the weight, as for each monomer component in 2 or more sets of monomer components of a different presentation used in order to obtain the above-mentioned acrylic block copolymer, it is desirable that it is the monomer component which contains an acrylic (meta) monomer 55% of the weight or more. It is 80 % of the weight or more most preferably.

[0034] As an example of the monomer component which Tg on count of the above-mentioned polymer becomes below -20 degrees C (253K) at least, the monomer component constituted by one sort, such as an ethyl acrylate, butyl acrylate, and 2-ethylhexyl acrylate, or two sorts or more is mentioned. Moreover, as an example of the monomer component from which Tg on count of the above-mentioned polymer becomes more than at least 70 degree C (343K), the monomer component constituted by one sort, such as an acrylic acid, a methacrylic acid, a methyl methacrylate, methacrylic-acid isopropyl, and cyclohexyl methacrylate, or two sorts or more is mentioned. Furthermore, if the combination of a desirable monomer component is mentioned especially, the combination of the monomer component which uses as a principal component the monomer component which uses butyl acrylate as a principal component, and a methyl methacrylate, the combination of the monomer component which uses as a principal component the monomer component which uses 2-ethylhexyl acrylate as a principal component, and a methyl methacrylate, and the combination of the monomer component which uses as a principal component the monomer component which uses 2-ethylhexyl acrylate as a principal component, and cyclohexyl methacrylate are mentioned.

[0035] As a desirable polymerization gestalt for obtaining the above-mentioned acrylic block copolymer, it is a radical polymerization, and solution polymerization and a bulk polymerization are desirable especially. This can make a homogeneous block polymer easy to obtain. As the block structure of the above-mentioned acrylic block copolymer, when triblock structure, the star type block structure, and a JI (meta) acrylic monomer and various cross linking agents are used, the multi-block structure from which these various block structures join together, and are acquired is mentioned, for example. It is desirable that they are the star type block structure and the multi-block structure which the star type block structure combined also in these. The star type block structure and the reason nil why the multi-block structure is desirable are that it becomes the thing excellent in mechanical physical properties since block effectiveness becomes good. It is the star type block structure and its multi-block structure, and by becoming that from which Tg of each block chain changed continuously or gradually, the vibration-deadening nature which was excellent in the large temperature requirement is shown, and mechanical physical properties are also most excellent. Moreover, it is desirable when the star type block structure is acquired by the polymerization using a tetravalent multiple-valued mercaptan.

[0036] As molecular weight of the above-mentioned acrylic block copolymer, it is desirable that weight average molecular weight is 10000-1 million for example. When there is a possibility that an acrylic block copolymer may be inferior to a mechanical strength or thermal resistance in it being less than 10000 and 1 million is exceeded, there is a possibility that un-arranging may arise in respect of molding workability, coating nature, etc. More preferably, it is 50000-500000 and such an acrylic block copolymer becomes what was very excellent also in which point of a mechanical strength, thermal resistance, molding workability, and coating nature. The above-mentioned weight average molecular weight means what is called for as standard polystyrene conversion with gel permeation chromatography (gel permeation chromatography, GPC).

[0037] About the transparency of the above-mentioned acrylic block copolymer, it may be transparent or may be opaque. Moreover, about the acrylic block-copolymer constituent which added various additives etc. to the above-mentioned acrylic block copolymer, similarly, it may be transparent or may be opaque. As criteria which distinguish whether it is transparent or opaque, if it distinguishes with parallel ray permeability for example, parallel ray permeability is transparent in it being 80% or more, and it is opaque in parallel ray permeability being less than 80%. In an acrylic block copolymer, when the compatibility of each block chain is not enough, or when bridge formation beyond a fixed limit is given, it may become opaque.

[0038] This invention is a constituent for sound deadeners which comes to contain the above-mentioned acrylic block copolymer further, and the content of the above-mentioned acrylic block copolymer is also the constituent for sound deadeners which is 10 % of the weight or more, when the above-mentioned constituent for sound deadeners is made into 100 % of the weight. The vibration-deadening engine performance of the high-damping material formed from the constituent for sound deadeners as it is less than 10 % of the weight will not become enough. It is 30 % of the weight or more, and more preferably, it is 50 % of the weight or more, and is 80 % of the weight or more. In such a constituent for sound deadeners, an acrylic block copolymer may use one sort and may use two or more sorts.

[0039] although the above-mentioned constituent for sound deadeners may contain only the acrylic block copolymer which is an indispensable component -- the need -- responding -- other components -- one sort -- or two or more sorts may be included. As a component besides the above, for example Various synthetic-rubber; polymethyl methacrylates, such as a natural rubber; styrene butadiene rubber, Various synthetic resin, such as polystyrene, polyolefine, and polyester; A styrene-butadiene-styrene block copolymer, various thermoplastic-elastomer, such as an ethylene-ethyl acrylate copolymer, -- bitumen matter [ , such as asphalt, ]; -- graphite -- Various fillers, such as a mica, carbon black, a calcium carbonate, talc, and clay; A natural fiber, Various oil, such as various plasticizer; silicone oils, such as various fiber; phthalic-acid octyls, such as a synthetic fiber, a glass fiber, and a metal fiber, and process oil; various flameproofing agents, such as a phosphoric-acid system flameproofing agent, a bromine system flameproofing agent, and an antimony trioxide, etc. are mentioned.

[0040] As a weight rate that a component besides the above occupies in the constituent for sound deadeners of this invention, if the constituent for sound deadeners is made into 100 % of the weight, it will become less than 90 % of the weight. Since an acrylic block copolymer decreases too much that it is 90 % of the weight or more, the vibration-deadening engine performance will fully be demonstrated. It is less than 70 % of the weight, and still more preferably, it is less than 50 % of the weight, and is less than 20 % of the weight most preferably.

[0041] the constituent for sound deadeners of this invention -- again -- the need -- responding -- various cross linking agents -- one sort -- or two or more sorts may be included. As such a cross linking agent, the compound which has two or more hindered amino groups is mentioned into molecules, such as various metal cross linking agent; tetrakis (2, 2, 6, and 6-tetramethyl-4-piperidyl) 1, 2, and 3, such as various multifunctional-compound; zinc oxides, such as a diepoxy compound and a diisocyanate compound, zinc acetate, magnesium acetate, aluminium acetate, and zinc stearate, and 4-butanetetra-carboxylate (a trade name "ADEKA stub LA-57", Asahi Denka Kogyo K.K. make), for example. If such a cross linking agent is used, the vibration-deadening engine performance and mechanical physical properties will improve by constructing a bridge over a polymer.

[0042] In using the above-mentioned cross linking agent, a functional group combinable with the above-mentioned cross linking agent is needed in the above-mentioned acrylic block copolymer. When the compound which is not limited especially as the combination, for example, has a diepoxy compound, various metal cross linking agents, and a hindered amino group as a cross linking agent is used, it is desirable to make it an acrylic block copolymer have a carboxyl group. Moreover, when a diisocyanate compound is used as a cross linking agent, it is desirable to make it an acrylic block copolymer have a hydroxyl group.

[0043] As a weight rate that the above-mentioned cross linking agent occupies in the constituent for sound deadeners of this invention, when the constituent for sound deadeners is made into 100 % of the weight, it is desirable to consider as less than 50 % of the weight. When it exceeds 50 % of the weight, the constituent for sound deadeners becomes hard too much, and there is a possibility of being hard that it may come to absorb vibrational energy. More preferably, it is less than 30 % of the weight, and is less than 20 % of the weight still more preferably.

[0044] It is not limited especially as a use gestalt of the constituent for sound deadeners of this invention, for example, the gestalt which, and makes the shape of a sheet, sticks on various base materials or is inserted between members is mentioned. [ carrying out a spray coating cloth to various base materials ] Although it will not be limited especially as thickness of the high-damping material formed from the constituent for sound deadeners of this invention but will be suitably chosen according to the purpose, it will use by 1 micrometer - 10cm usual. It is not limited especially as the various above-mentioned base materials or a member, for example, metal plates, such as various steel plates, various plywoods, a gypsum plate, various resin plates, a fiber strengthening resin plate, a cement product, precast concrete, a mortar product, etc. can be used.

[0045] And it is the manufacture approach of the acrylic block copolymer which comes to contain the \*\*\*\*\* reaction process which gives 2 or more sets of monomer components of a different presentation to a polymerization reaction under existence of the multiple-valued mercaptans more than trivalent. this invention -- The maximum difference of the glass transition point on count of each acrylic polymer obtained when 2 or more sets of monomer components of a presentation different the account of a top carry out the polymerization of each monomer component (Tg) is 130-200 degrees C. The weight of the monomer component from which the polymer with which Tg on count becomes 50 degrees C or more is obtained is 35 - 65% of the weight of the rate of occupying to 100 % of the weight of AUW of all monomer components. The above-mentioned polymerization reaction process While the conversion of the \*\*\*\*\* component first given to a polymerization reaction is less than 45%, the monomer component first given to the polymerization reaction is also the manufacture approach of the acrylic block copolymer performed considering \*\*\*\*\* which gives the different following monomer component to a polymerization reaction as indispensable.

[0046] The compound which made the hydrogen sulfide add to the compound; multiple-valued epoxy compound which has three or more sulfhydryl groups, such as a polyester ghost; TORICHIO glycerol of the compound which is not limited especially as multiple-valued mercaptans more than trivalent [ above-mentioned ], for example, has three or more hydroxyl groups, such as trimethylol propane, such as pentaerythritol tetrakis thioglycolate (PETG), and pentaerythritol, and the mercaptans which have a carboxyl group; the mercaptoethanol esterification object of a multiple-valued carboxylic acid etc. is mentioned. These may be used independently and may use two or more sorts together. It is pentaerythritol tetrakis thioglycolate (PETG) which is tetravalent mercaptans most preferably also in these. The block copolymer which the generation effectiveness of an acrylic block copolymer becomes it high that they are tetravalent mercaptans, and has star type structure will be obtained. Since the molecular weight of the acrylic block copolymer to generate serves as suitable range as amount of such mercaptans used, it is desirable to consider as 0.1 - 10 % of the weight to 100 % of the weight of all monomer components.

[0047] As a monomer used at the polymerization reaction process in the manufacture approach of the above-mentioned acrylic block copolymer, it is the same with having mentioned above, for example, one sort, such as an acrylic acid (meta), acrylate (meta), diacrylate, and a styrene system monomer, or

two sorts or more are mentioned, and when all the repeat units of the acrylic block copolymer to generate are made into 100 % of the weight, it is desirable to set up so that the repeat unit formed of an acrylic (meta) monomer may become 55 % of the weight or more. Moreover, it is the same with having mentioned the desirable polymerization gestalt above, and they are solution polymerization and a bulk polymerization. It is simple for it not to be limited especially as polymerization equipment, for example, to use a tank reactor, a tubing type reactor, a cast polymerization, a notes form polymerization, etc., and it is desirable.

[0048] It is desirable to consider as -100-200 degrees C as polymerization temperature at the above-mentioned polymerization reaction process. Since it can manufacture economically with a simple facility more preferably, it is considering as 50-150 degrees C. Moreover, it is not indispensable to use an initiator. For example, in the case where a polymerization is performed at an elevated temperature, it is because an acrylic block copolymer can be manufactured only by the thermal polymerization of a monomer component and mercaptans, without using an initiator. On the other hand, a polymerization may be performed using a general azo system initiator or a peroxide system initiator. As such an initiator, 2 and 2'-azobis (2-methyl butyronitrile), benzoyl peroxide, etc. are mentioned, for example. These may be used independently and may use two or more sorts together.

[0049] In the manufacture approach of the above-mentioned acrylic block copolymer, three points, next (Ha), (d), and (e), are mentioned the most important in order to do the operation effectiveness of this invention so. Namely, (Ha), the thing for which 2 or more sets of monomer components of a different presentation from which the maximum difference of the glass transition point (Tg) of the polymer obtained when the polymerization of each monomer component is carried out becomes 130 degrees C or more are used, The weight of the \*\*\*\*\* component given to the (d) beginning at a polymerization reaction is 35 - 65% of the weight of the rate of occupying to 100 % of the weight of AUW of all monomer components, While the conversion of the monomer component given to the (e) beginning at the polymerization reaction is less than 45%, the monomer component first given to the polymerization reaction is \*\*\*\*\* which gives the different following monomer component to a polymerization reaction. A polymerization reaction process will be performed using such requirements for three points as indispensable.

[0050] In the above-mentioned polymerization reaction process, while the conversion (henceforth "initial conversion") of the \*\*\*\*\* component first given to a polymerization reaction is less than 45%, it becomes \*\*\*\*\* which gives the different following monomer component from the monomer component first given to the polymerization reaction to a polymerization reaction. When initial conversion exceeds 45%, the copolymer block chain which has in-between Tg in which the mixture of the \*\*\*\*\* component first given to a polymerization reaction and the other dropped monomer component carries out a polymerization, and which it generates will decrease, and the vibration-deadening engine performance in the temperature field will fall. Moreover, when generating the polymer block chain which has Tg with the high \*\*\*\*\* component first given to a polymerization reaction, it is desirable that initial conversion is 10% or more. In this case, since the block chain which has high Tg as initial conversion is less than 10% decreases too much, the cohesive force of an acrylic block copolymer becomes weak, and there is a possibility that a mechanical strength, vibration-deadening engine performance, etc. of a high-damping material may fall. It is 20 - 40% more preferably. In addition, initial conversion is the weight of the \*\*\*\*\* component first given to a polymerization reaction T1 It is the weight of the monomer component which carried out, among these carried out the polymerization T2 If it carries out, it can ask by  $x(T2 / T1) 100$ .

[0051] Although \*\*\*\*\* given to a polymerization reaction by dropping a monomer component at a polymerization system at the above-mentioned polymerization reaction process is desirable, as drop time, it is desirable to consider as 30 - 600 minutes for example. If dropped more quickly than 30 minutes, when the polymerization will advance at the rate of usual, only the block chain with which time amount for the block chain which has in-between Tg to generate is formed from the component near [ it will be too few and ] the mixture of the \*\*\*\*\* component first given to a polymerization reaction and the monomer component dropped at a degree will generate in a large quantity. That is, since it

becomes impossible to advance a polymerization, changing the monomer presentation in a polymerization system continuously or gradually, when the temperature width of face of Tg of an acrylic block copolymer becomes narrow, there is a possibility that operating temperature limits may become narrow.

[0052] In the above-mentioned polymerization reaction process, although 2 or more sets of monomer components of a different presentation are used, as a gestalt of 2 or more sets of monomer components of such a different presentation, it is the same with having mentioned above. Moreover, a monomer component with higher Tg on count of the polymer obtained when the polymerization of 2 or more sets of monomer components of a different presentation is carried out (A), When a polymerization is carried out and Tg on count of the polymer obtained divides into the monomer component (B) of the lower one, as weight rate [ of a monomer component (A) and a monomer component (B) ] (A)/(B), it is 35 / 65 - 65/35, and is 40 / 60 - 60/40 still more preferably. (A) It becomes easy to make the block chain which has each Tg from Tg of such a high side that / (B) is close to 50/50 to Tg of a low side generate uniformly. In addition, it is desirable to divide all the monomer components whose Tg(s) on count of the polymer obtained when Tg on count of the polymer obtained when a polymerization is carried out uses as a monomer component (A) all the monomer components that are 50 degrees C or more and carries out a polymerization in order to divide into a monomer component (A) and a monomer component (B) for example, are less than 50 degrees C as a monomer component (B). a monomer component (A) and (B) -- the rate near 50/50 -- using -- in addition -- and the polymer in which high tandelta is shown for the first time in a broad temperature requirement is obtained by making initial conversion 45% or less.

[0053] Although not limited especially as \*\*\*\*\* which gives 2 or more sets of monomer components of a presentation different the account of a top to a polymerization reaction, \*\*\*\*\* which gives first the monomer component from which the polymer which has for example highest Tg is obtained to a polymerization reaction is desirable. Tg becomes being easy to carry out specified quantity generation of the highest block chain by this, it will originate in a block chain with highest Tg existing above to some extent in an acrylic block copolymer, the cohesive force as the whole polymer will increase, and a mechanical strength, thermal resistance, etc. will improve. Moreover, \*\*\*\*\* which trickles the monomer component from which the polymer which has lowest Tg is obtained at the end, and is given to a polymerization reaction is desirable. Tg becomes being easy to carry out specified quantity generation of the lowest block chain by this, it will originate in a block chain with lowest Tg existing above to some extent in an acrylic block copolymer, the flexibility as the whole polymer will increase, and cold resistance will improve.

[0054] By the manufacture approach of the above-mentioned acrylic block copolymer, while a loss tangent (tandelta) is -50-150 degrees C, the acrylic block copolymer of this invention which is 0.3 or more can be produced easily and efficiently over temperature width of face of 90 degrees C or more. Therefore, by such manufacture approach, it can cross to a broad temperature requirement, the vibration-deadening engine performance more than fixed can always be shown, and the operation effectiveness of the acrylic block copolymer of this invention which can be made to apply broadly in various kinds of fields can be made more fully demonstrated.

[0055]

[Example] Although an example is given to below and this invention is further explained to a detail, this invention is not limited only to these examples. In addition, among an example, especially, as long as there is no notice, the "section" means the "weight section."

[0056] The monomer component (A1) which becomes the glass reactor of example 1 capacity 2L from the methyl-methacrylate (MMA) 267.3 section, the acrylic-acid (AA) 2.7 section, and the ethyl-acetate 240 section was taught, and it heated with the 90-degree C water bath under nitrogen-gas-atmosphere mind, stirring. It supplied in the place where internal temperature became fixed, having initiator covered [ which consists of the 2 and 2'-azobis (2-methyl butyronitrile) 0.6 section, the trimethylol propane tris (3-mercaptopropionate) 6.0 section, and the ethyl-acetate 30 section ] it for 5 minutes, and the polymerization was made to start.

[0057] After [ of polymerization initiation ] 60 minutes, dropping of the monomer component (B1)

which consists of the butyl acrylate (BA) 326.7 section, the AA3.3 section, and the ethyl-acetate 300 section was started, and the polymerization was advanced succeeding in the place where conversion became 31.1%. Dropping was ended after [ of polymerization initiation ] 180 minutes (after [ of dropping initiation ] 120 minutes), and the polymerization was advanced as it is. The initiator solution for aging which becomes each 240 minutes 210 minutes after polymerization initiation and after polymerization initiation from the 2 and 2'-azobis (2-methyl butyronitrile) 0.6 section and the ethyl-acetate 15 section was thrown in, and the polymerization was advanced further.

[0058] By cooling after [ of polymerization initiation ] 360 minutes, the polymerization was completed and the acrylic block-copolymer solution was obtained. The conversion at this time was 96.0%. About the obtained acrylic block copolymer, the determination of molecular weight, dynamic viscoelasticity measurement, and a hauling trial were performed by the following approach. A result is shown in Table 1.

[0059] Using the high-speed-gel-permeation-chromatography system "HLC-8120GPC" (trade name) by determination-of-molecular-weight TOSOH CORP., using THF as an expansion solvent, 0.1%THF solution of an acrylic block copolymer was poured in, and it measured. Number average molecular weight (Mn) and weight average molecular weight (Mw) are shown in Table 1.

[0060] the dynamic viscoelasticity measurement profit \*\*\*\* acrylic block-copolymer solution was dried with the 200-degree C vacuum drier for 6 hours, and the sheet without a bubble with a thickness of 4mm was obtained. Press molding of this sheet is carried out at 100 degrees C, and it considers as a 2mm sheet, and is \*\*\*\*\* about a test piece with a diameter of 7.9mm after this. He is REOMETO Rix about this test piece. The sample base of the dynamic viscoelasticity measuring instrument "RDAII" (trade name) by the Far East company was pasted, and it measured by part for frequency [ of 10Hz ], strain [ of 0.2% ], and programming-rate/of 3 degrees C. The temperature requirement of tandelta is shown in Table 1.

[0061] Hauling trial JIS It measured according to K6251 "the hauling test method of vulcanized rubber." That is, it examined by part for 500mm/in hauling rate under the ambient atmosphere of three-piece \*\*\*\* omission, 23 degrees C, and 65%RH from the sheet with a thickness of 2mm which mentioned above the test piece of a dumbbell-like No. 2 form, and tensile strength and the average of elongation were calculated. A result is shown in Table 1.

[0062] The monomer component (A2) which consists the 267.3 sections and AA of the 2.7 sections and the ethyl-acetate 240 section in MMA was taught to the glass reactor of example 2 capacity 2L, and it heated with the 90-degree C water bath under nitrogen-gas-atmosphere mind, stirring. It supplied in the place where internal temperature became fixed, having initiator covered [ which consists of the 2 and 2'-azobis (2-methyl butyronitrile) 0.6 section, the PETG6.0 section, and the ethyl-acetate 30 section ] it for 5 minutes, and the polymerization was made to start.

[0063] After [ of polymerization initiation ] 60 minutes, dropping of the monomer component (B-2) which consists of the BA326.7 section, the AA3.3 section, and the ethyl-acetate 300 section was started, and the polymerization was advanced succeeding in the place where conversion became 34.3%. Dropping was ended after [ of polymerization initiation ] 180 minutes (after [ of dropping initiation ] 120 minutes), and the polymerization was advanced as it is. The initiator solution for aging which becomes each 240 minutes 210 minutes after polymerization initiation and after polymerization initiation from the 2 and 2'-azobis (2-methyl butyronitrile) 0.6 section and the ethyl-acetate 15 section was thrown in, and the polymerization was advanced further. By cooling after [ of polymerization initiation ] 360 minutes, the polymerization was completed and the acrylic block-copolymer solution was obtained. The conversion at this time was 96.0%. Desiccation of a polymer, GPC measurement, dynamic viscoelasticity measurement, and a hauling trial were performed like the example 1. A result is shown in Table 1.

[0064] The monomer component (A3) which becomes about the 264.6 sections in MMA and becomes the glass reactor of example 3 capacity 2L from the 2.7 sections and the ethyl-acetate 240 section about the 2.7 sections and tetraethylene glycol diacrylate in AA was taught, and it heated with the 90-degree C water bath under nitrogen-gas-atmosphere mind, stirring. Internal temperature - It supplied in the place



used as a law, having initiator covered [ which consists of the 2 and 2'-azobis (2-methyl butyronitrile) 0.6 section, the PETG6.0 section, and the ethyl-acetate 30 section ] it for 5 minutes, and the polymerization was made to start.

[0065] After [ of polymerization initiation ] 60 minutes, dropping of the monomer component (B3) which consists of the BA326.7 section, the AA3.3 section, and the ethyl-acetate 300 section was started, and the polymerization was advanced succeedingly in the place where conversion became 34.3%. Dropping was ended after [ of polymerization initiation ] 180 minutes (after [ of dropping initiation ] 120 minutes), and the polymerization was advanced as it is. The initiator solution for aging which becomes each 240 minutes 210 minutes after polymerization initiation and after polymerization initiation from the 2 and 2'-azobis (2-methyl butyronitrile) 0.6 section and the ethyl-acetate 15 section was thrown in, and the polymerization was advanced further. By cooling after [ of polymerization initiation ] 360 minutes, the polymerization was completed and the acrylic block-copolymer solution was obtained. The conversion at this time was 96.0%. Desiccation of an acrylic block copolymer, GPC measurement, dynamic viscoelasticity measurement, and a hauling trial were performed like the example 1. A result is shown in Table 1 and drawing 1.

[0066] After adding the ADEKA stub LA-57 (trade name, Asahi Denka Kogyo K.K. make) 0.7 section which is hindered amine and mixing in the acrylic block-copolymer solution 50 section of example 4 example 3, the constituent for sound deadeners (ion bridge formation object) which comes to contain an acrylic block copolymer was obtained by drying like an example 1. About this bridge formation object, desiccation, GPC measurement, dynamic viscoelasticity measurement, and a hauling trial were performed like the example 1. A result is shown in Table 1.

[0067] The monomer component (comparison A1) which becomes the same equipment as example of comparison 1 example 1 from the styrene 250 section, the MMA250 section, and the butyl-acetate 250 section was taught, and it heated with the 110-degree C oil bath under nitrogen-gas-atmosphere mind, stirring. The dipentaerythritol hexa kiss thiopropionate 10 section and the butyl-acetate 50 section were supplied, and the polymerization was made to start in the place where temperature became fixed. The polymerization was advanced after [ of polymerization initiation ] 20 minutes, applying for 180 minutes and being dropped [ the monomer component (comparison B1) which consists of the ethyl-acrylate 475 section and the methacrylic-acid 25 section begins to be dropped, and ] as it is, in the place where conversion became 5.5% till polymerization initiation 200 minutes. After dropping termination, after continuing the polymerization for further 3 hours, it cooled, and the block-copolymer solution was obtained. Desiccation of a block copolymer, GPC measurement, dynamic viscoelasticity measurement, and a hauling trial were performed like the example 1. A result is shown in Table 1.

[0068]

[Table 1]



| 項目  | 実施例1       | 実施例2        | 実施例3        | 実施例4        | 比較例1     |
|---|------------|-------------|-------------|-------------|----------|
| Mn (万)  | 1.1        | 1.3         | 1.8         | 1.8         | 8.9      |
| Mw (万)  | 8.3        | 9.5         | 17.4        | 17.4        | 72.1     |
| 初期仕込みの単量体混合物(A)から得られる重合体の計算上のT <sub>g</sub> (°C)  | 105        | 105         | 105         | 105         | 102      |
| 滴下した単量体混合物(B)から得られる重合体の計算上のT <sub>g</sub> (°C)    | -50        | -50         | -50         | -50         | -19      |
| 単量体混合物(A)、(B)から得られる重合体の計算上のT <sub>g</sub> の差 (°C) | 155        | 155         | 155         | 155         | 121      |
| 単量体混合物(A)、(B)の重量比(A/B)                            | 45/55      | 45/55       | 45/55       | 45/55       | 50/50    |
| tan $\delta$ が0.3以上となった温度範囲 (°C)                  | -8~<br>129 | -11~<br>134 | -15~<br>140 | -27~<br>140 | 5~<br>90 |
| tan $\delta$ が0.3以上となった温度幅                        | 137        | 145         | 155         | 167         | 85       |
| 引っ張り強度 (MPa)                                      | 1.06       | 1.63        | 2.37        | 3.45        | 5.75     |
| 引っ張り伸び率 (%)                                       | 1630       | 1410        | 1027        | 1010        | 314      |

[0069] The acrylic block copolymer in which physical properties as shown in Table 1 are shown according to the polymerization process shown in the examples 1-4 was able to be obtained easily. Practicality of the acrylic block copolymer of an example 1 and an example 2 is improving remarkably in that the temperature requirement which the temperature width of face from which  $\tan \delta$  which is the index of the vibration-deadening engine performance became 0.3 or more is large, and can use as a sound deadener 50 degrees C or more from the block copolymer of the example 1 of a comparison spread sharply. Since breadth and tensile strength are also increasing [ the temperature width of face from which  $\tan \delta$  became 0.3 or more ] further, practicality of the acrylic block copolymer of an example 3 and an example 4 is improving further.

[0070]

[Effect of the Invention] Since the acrylic block copolymer of this invention consists of an above-mentioned configuration, is crossed to a broad temperature requirement and always shows the vibration-deadening engine performance more than fixed, it is a block copolymer which the practicality of a high-damping material can be raised remarkably and can be broadly used in that the temperature requirement which can be used as a high-damping material can be extended sharply in various kinds of fields, such as an automobile, a building, a vessel, and electrical and electric equipment. Moreover, the acrylic block copolymer of this invention is efficiently [ easily and ] producible by the manufacture approach of the acrylic block copolymer of this invention.

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[Translation done.]